

Directions for Further Development of GaAs/CuInSe₂ Thin Film Tandem Cells

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Summary

Multijunction thin film solar cells utilizing GaAs and CuInSe₂ as semiconductor absorbers are rapidly developing, becoming a viable technology for space power systems with an unparalleled combination of high efficiency, low mass, and high radiation tolerance. The prospect for evolutionary improvement of this type of cell towards efficiency of $\approx 30\%$ and specific power greater than 1 kW/kg while retaining the attribute of high radiation tolerance are good. Limitations of the present configuration and possible avenues for circumventing these problems are presented.

Introduction

In the nine years since the first demonstration of both thin film CuInSe₂ cells and the CLEFT process for fabricating thin film single crystals of GaAs, tremendous strides have been made in the maturation of both technologies. Each has been shown capable of fabricating large-area films [refs. 1 & 2] of high quality as attested to by the recent achievement of tandem efficiency greater than 20% AM0. Bereft of excess high density semiconductor bulk, the practical lower mass limit for these cells is determined by their support structures, shifting the focus of mass reduction efforts to the module, panel, and array level designs. It is the conjunction of this inherently low mass with both high efficiency and high radiation tolerance, however, which enables the array designer to capitalize on this asset, since the array size may be smaller relative to other options and still guarantee adequate End-Of-Life (EOL) system power.

Although there is little benefit at the systems level of further reducing the *direct* cell mass, improvements in EOL specific power may still be achievable by reducing mass contributions of associated components, increasing Beginning-Of-Life (BOL) efficiency, and increasing radiation tolerance. The remainder of this paper will comprise a discussion of means by which this may be achieved.

Bandgap Engineering of AlGaAs/CuInSe₂ Tandem Cells

CuInSe₂ is a ternary chalcopyrite semiconductor, which unlike the ternary alloy of AlAs and GaAs, Al_xGa_{1-x}As, has a fixed bandgap (to first order). Its attributes that commend its use in space photovoltaics include one of the highest known absorption coefficients of any semiconductor [ref. 3], an optimum bandgap for the lower cell in two-junction tandems [ref. 4], and an exceptional tolerance to high-energy particulate radiation [ref. 5]. In a heterojunction with CdZnS it has shown excellent minority carrier collection, achieving internal quantum efficiencies nearing unity [ref. 6]. Its greatest liability is the low voltage of the cell compared to its bandgap. Conventional diffusion-current dominated ideal photodiodes with this bandgap would be predicted to exhibit open-circuit

voltages as high as ≈ 560 mV [ref. 7] at comparable current levels to those of $\text{CuInSe}_2/\text{CdZnS}$ in tandem with GaAs, compared to an observed $V_{oc} \approx 380$ mV. The reasons for this low voltage are an active area of research and debate in the literature, but it is most likely due to interface states acting as a recombination pathway for minority carriers [ref. 8 and 9], with deep level defects in the bulk possibly playing a role [ref. 10]. Improvements in CuInSe_2 cell voltage are most likely to result from refinement of the component materials and their fabrication processes. Certainly *any* success in improving the voltage performance of CuInSe_2 cells will contribute to the overall performance of the tandem. In practice this plays a crucial role, however, in selection of the optimum bandgap for the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ upper cell.

Hybrid Tandem Cells

The present state-of-the-art thin film solar cells are hybrid or mechanically stacked, each component cell fabricated independently before being incorporated into the tandem. There are numerous advantages to this approach, foremost being *flexibility*. A range of bandgaps for upper and lower cell are possible, permitting their design to be tailored to the requirements of the mission and properties of the available materials. Other advantages include series/parallel buss interconnect flexibility and less sensitivity to temperature effects on orbit. The principal disadvantage of hybrid tandems is the increased complexity of fabrication and interconnection concomitant with its increased flexibility.

Previously published calculations [Table 1 in ref. 11] for $\text{Al}_x\text{Ga}_{1-x}\text{As}$ *shallow homojunction* cells in four-terminal tandem configuration with CuInSe_2 cells showed minor ($\leq 0.7\%$) losses in BOL efficiency for increasing $x \leq 0.3$ though it still remained over 22% in all cases. This was due in part to assumptions regarding minority carrier lifetimes in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ subsequently shown to be overly pessimistic [ref. 12]. This was also a consequence, however, of the upper cell with increased bandgap losing current to the lower cell operating at less than ideal voltage. These considerations indicate that the aluminum content (x -value) that maximizes BOL efficiency for $\text{Al}_x\text{Ga}_{1-x}\text{As}/\text{CuInSe}_2$ tandems is less than the theoretical optimum of $x \approx 0.3$ calculated for ideal cells in reference 4. Radiation degradation effects, however, provide a countervailing influence on the optimum choice of aluminum content in the upper $\text{Al}_x\text{Ga}_{1-x}\text{As}$ cell for four-terminal tandem operation. Since both CuInSe_2 and $\text{Al}_x\text{Ga}_{1-x}\text{As}$ cells are more radiation resistant than GaAs cells [refs. 5, 13, and 14], and available data suggest that the radiation effects in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ are less severe for higher aluminum content [refs. 15 and 12] in the range $x \leq 0.37$, EOL efficiency maximization *for many missions* will increase the optimum value of x over the optimum for BOL efficiency.

Another available path for improved efficiency in the hybrid tandem configuration is the use of a monolithic $\text{Al}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ tandem cell mechanically stacked on a CuInSe_2 cell. The choice of bandgaps is near optimum in this case for $x \approx 0.4$ [ref. 4], and practical efficiencies near 30% should be achievable.

Monolithic Thin Film Tandem Cells

Certain components to the successful fabrication of high efficiency monolithic tandems appear important. Current matching (at some optimum point in the mission lifetime) is necessary. The calculations reported in reference 11 predict BOL current matching at an upper cell absorber layer composition near $\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$, a modest aluminum content for which high quality films should be

readily achievable. Fabrication of an Intercell Ohmic Contact (IOC) is one of the persistently vexing difficulties in the fabrication of monolithic tandem cells. One solution used successfully in references 16 and 17 has been fabrication of a tunnel junction between upper and lower cells, but steps must be taken to avoid interdiffusion at the highly-doped, abrupt interface which can result in a resistive, highly compensated transition region which destroys the tunnel junction.

The lattice mismatch between CuInSe_2 and GaAs is less than 2% and the chalcopyrite symmetry of CuInSe_2 is a ternary equivalent of two GaAs zincblende crystal unit cells distorted slightly along the connecting c-axis. Heteroepitaxial single-crystal cell structures in material systems with comparable or greater amounts of lattice mismatch have been widely pursued, utilizing the techniques of advanced epitaxial growth technology such as graded composition lattice-matching transition layers and superlattice dislocation propagation filters. Given the nearly perfect carrier collection efficiency in *polycrystalline* CuInSe_2 cells, it appears that the minority-carrier electron transport in the material is tolerant of the native defects in the material. This may relax the requirement for crystalline perfection compared to III-V based materials. Study of the epitaxial growth of CuInSe_2 on GaAs has been reported in reference 18 and references therein.

I propose a novel solution [ref. 19] to these problems which capitalizes on the unique abilities of the CLEFT process and properties of the constituent materials. Figure 1 shows a cross-sectional schematic of the proposed structure. Fabrication is begun by the overgrowth of a GaAs CLEFT buffer on a GaAs wafer. Next, the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ cell is fabricated in an 'inverted' configuration with the emitter nearest the buffer. Since this is the first device structure deposited, it can be deposited at high temperature to improve the quality of the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ without degrading the tunnel junction. The proposed tunnel junction is formed between a $p^+-\text{Al}_x\text{Ga}_{1-x}\text{As}$ and subsequently deposited $n^+-\text{ZnSe}$ layer. This ZnSe layer is compositionally and dopant graded to form an $n\text{-CdZnSSe}$ contact to the final semiconductor $p\text{-CuInSe}_2$ absorber layer. Back contacts are deposited, the film is cleaved from the bulk GaAs wafer, front contacts formed and the excess buffer layer removed before AR coating completes the device.

The technology for fabrication of the tunnel junction has only recently been demonstrated, although to the author's knowledge it has not yet been done. High-quality single-crystal ZnSe and GaAs lattice-matched $\text{Zn}_{0.05}\text{Se}_{0.95}$ can be deposited on GaAs or $\text{Al}_x\text{Ga}_{1-x}\text{As}$ by numerous processes including MBE [ref. 20] and MOCVD [ref. 21]. Recently, effective doping of ZnSe, long an elusive goal of research, has been demonstrated [ref. 22]. In fact, degenerate doping of ZnSe to levels of $2.8 \times 10^{19} \text{cm}^{-3}$ with Hall mobilities of $140 \text{cm}^2/\text{V}\cdot\text{s}$ and resultant resistivity of $10^{-3} \Omega\cdot\text{cm}$ have been reported at a temperature of 318°C [ref. 23], quite adequate for tunnel junction fabrication without significant interdiffusion. Though a reliable direct measurement of the ZnSe/GaAs conduction band offset is unavailable, application of the theory of Tersoff in reference 24 predicts a valence band offset of 0.04 volts, essentially zero within the accuracy of the theory, though this calculation is only thought to be accurate to within ≈ 0.15 volts. Certainly recent evidence suggests that the density of interfacial surface states between ZnSe and GaAs can be very low [ref. 25].

Perhaps the greatest challenge in fabricating the monolithic $\text{Al}_x\text{Ga}_{1-x}\text{As}/\text{CuInSe}_2$ tandem is the formation of a high-quality heterojunction between the CdZnSSe interconnect region and the subsequently deposited CuInSe_2 absorber. The results reported in reference 18 for deposition of epitaxial single crystal CuInSe_2 on GaAs suggest that careful control of composition can produce p-type films without a Cu-rich second phase which appears to minimize Cu out-diffusion. This is important since Cu forms a deep level trap in the ZnSe, ZnS, and CdS binary constituents of the interconnect alloy. It would appear from this previous work that the key to successful fabrication of this device is the development of a lower temperature process for the fabrication of high quality CuInSe_2 than

the elemental codeposition process presently employed. Given the widespread technological effort to develop lower temperature processes for the deposition of other important semiconductor materials, usually for the same reason of minimizing interdiffusion in multilayered structures, I believe the solution of this problem to be feasible.

References

- [1] R.A. Mickelsen, B.J. Stanbery, J.E. Avery, Wen S. Chen and W.E. Devaney, "Large Area CuInSe₂ Thin Film Solar Cells", *Conference Record 19th IEEE Photovoltaic Specialists Conference*, IEEE, 1987, pp.744-748.
- [2] R.P. Gale, B.D. King and J.C.C. Fan, "Large-Area GaAs CLEFT Layers for Solar Cell Applications", *Conference Record 19th IEEE Photovoltaic Specialists Conference*, IEEE, 1987, pp.293-295.
- [3] A.M. Hermann, L. Fabick, K. Zweibel and R. Hardy, "Progress in Polycrystalline Thin-film Photovoltaic Device Research", *Conference Record 16th IEEE Photovoltaic Specialists Conference*, IEEE, 1982, pp.840-845.
- [4] John C.C. Fan, B-Y. Tsaur and B.J. Palm, "Optimal Design of High-efficiency Tandem Cells", *Conference Record 16th IEEE Photovoltaic Specialists Conference*, IEEE, 1982, pp.692-701.
- [5] R.A. Mickelsen, Wen S. Chen, B.J. Stanbery, H. Dursch, J.M. Stewart, Y.R. Hsiao and W. Devaney, "Development of CuInSe₂ Cells for Space Applications", *Conference Record 18th IEEE Photovoltaic Specialists Conference*, IEEE, 1985, pp.1069-1073.
- [6] W.E. Devaney, R.A. Mickelsen and W.S. Chen, "Recent Improvements in CuInSe₂/ZnCdS Thin Film Solar Cell Efficiency", *Conference Record 18th IEEE Photovoltaic Specialists Conference*, IEEE, 1985, pp.1733-1734.
- [7] A.M. Barnett, S.L. Rhoads and G.H. Negley, "A Three Solar Cell Mechanical Stack with an AM0 Efficiency Greater than 30%", *Conference Record 19th IEEE Photovoltaic Specialists Conference*, IEEE, 1987, pp.1526-1527.
- [8] W.A. Miller and L.C. Olsen, *IEEE Trans. Electron Devices* **31**, 654 (1984).
- [9] C. Goradia, M. Goradia and R. Lopez, "On the Possible Enhancement of Open Circuit Voltage in n-(Cd,Zn)S/p-CuInSe₂ Polycrystalline Thin Film Solar Cells", *Conference Record 18th IEEE Photovoltaic Specialists Conference*, IEEE, 1985, pp.1399-1404.
- [10] Evangelos C. Demetriou and Allen Rothwarf, "An Admittance Study of the CuInSe₂/CdS Solar Cell", *Conference Record 19th IEEE Photovoltaic Specialists Conference*, IEEE, 1987, pp.764- 769.
- [11] B.J. Stanbery, J.E. Avery, R.M. Burgess, W.S. Chen, W.E. Devaney, D.J. Doyle, R.A. Mickelsen, R.W. McClelland, B.D. King, R.P. Gale and John C.C. Fan, "Thin Film Tandem GaAs/CuInSe₂ Solar Cells for Space Power Applications", *Conference Record 19th IEEE Photovoltaic Specialists Conference*, IEEE, 1987, pp.280-284.
- [12] R.K.Ahrenkiel, D. Greenberg, D.J. Dunlavy, T. Hanak, J. Schlupmann, H.C. Hamaker and C.R. Lewis, "Minority-Carrier Properties of 1.93-eV Al_xGa_{1-x}As Grown by MOCVD", *Conference Record 19th IEEE Photovoltaic Specialists Conference* IEEE, 1987, pp.1180-1186.
- [13] H.B. Curtis, C.K. Swartz, and R.E. Hart, Jr., "Radiation Performance of AlGaAs and InGaAs Concentrator Cells and Expected Performance of Cascade Structures. *Conference Record 19th IEEE Photovoltaic Specialists Conference*, IEEE, 1987, pp.727-732.

- [14] H.C. Hamaker, J.G. Werthen, C.R. Lewis, H.F. MacMillan, C.W. Ford, G.F. Virshup, R.K. Ahrenkiel, D.L. Greenberg and J. Schlupmann, "Radiation Damage of 1.93-eV $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and GaAs Solar Cells Grown By Metalorganic Chemical Vapor Deposition", *Conference Record 19th IEEE Photovoltaic Specialists Conference*, IEEE, 1987, pp.733-736.
- [15] Sheng S. Li, C.G. Choi and R.Y. Loo, "Studies of Radiation-Induced Defects in One-MeV and Low Energy Proton Irradiated Germanium and $\text{Al}_x\text{Ga}_{1-x}\text{As}$ P-N Junction Solar Cells", *Conference Record 18th IEEE Photovoltaic Specialists Conference*, IEEE, 1985, pp.640-645.
- [16] Masafumi Yamaguchi, Chikara Amano, Hideo Sugiura and Akio Yamamoto, "High Efficiency AlGaAs -GaAs Tandem Solar Cells with Tunnel Junction", *Conference Record 19th IEEE Photovoltaic Specialists Conference*, IEEE, 1987, pp.1484-1485.
- [17] Chikara Amano, Hideo Sugiura, Koshi Ando and Masafumi Yamaguchi, "High-efficiency $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ Solar Cells Grown by Molecular Beam Epitaxy", *Appl. Phys. Lett.* **51** (14), 5 October 1987, pp. 1075-1077.
- [18] E.R. Don, G.J. Russell and R. Hill, "RHEED Studies of CuInSe_2 Epitaxial Films", *Conference Record 18th IEEE Photovoltaic Specialists Conference*, IEEE, 1985, pp.1060-1064.
- [19] B.J. Stanbery, "Single Crystal, Heteroepitaxial, GaAlAs / CuInSe_2 Tandem Solar Cell and Method of Manufacture", U.S.S.N. 072,316 (1987).
- [20] B.J. Skromme, M.C. Tamargo, J.L. de Miguel and R.E. Nahory, "Photoluminescence Characterization of Heteroepitaxial ZnSe/GaAs and ZnSe/AlAs Grown by MBE Epitaxy of Semiconductor Layered Structures", *Materials Research Society Symposium Proceedings of the 1987 Fall Meeting* (in press).
- [21] A. Kamata, K. Hirahara, M. Kawachi and T. Beppu, "Lattice Matched Epitaxial Growth of ZnSSe on GaAs by MOCVD", *Extended Abstracts of the 17th Conference on Solid State Devices and Materials*, Tokyo, 1985, pp. 233-236.
- [22] T. Yao, *J. Crystal Growth*, **72**, 1985, p. 31.
- [23] T. Hariu, S. Yamaguchi, S. Goto, K. Shida and K. Matsushita, "Highly Conductive ZnSe Layers by Plasma-Assisted Epitaxy", *Extended Abstracts of the 18th (1986 International) Conference on Solid State Devices and Materials*, Tokyo, 1986, pp. 639-642.
- [24] J. Tersoff, "Summary Abstract: Failure of the common anion rule for lattice-matched heterojunctions", *J. Vac. Sci Technol. B* **4** (4), Jul/Aug 1986, pp. 1066-1067.
- [25] D.J. Olego, "Effects of ZnSe Epitaxial Growth on the Surface Properties of GaAs", *Appl. Phys. Lett.* **51** (18), 2 November 1987, pp. 1422-1424.

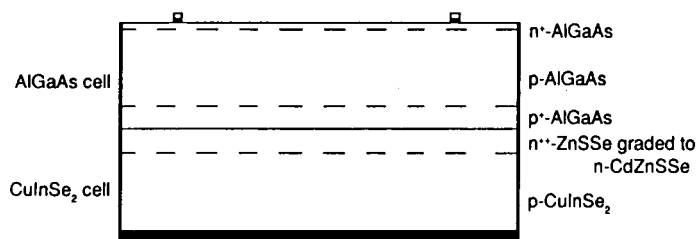


Figure 1.- Schematic of monolithic AlGaAs/CuInSe_2 cell.